

(NASA-TM-82414) SOLAR ENERGY ABSORPTION
CHARACTERISTICS AND THE EFFECTS OF HEAT ON
THE OPTICAL PROPERTIES OF SEVERAL COATINGS
(NASA) 14 p HC A02/MF A01 CSCL 10A

NO 1-22474

Unclass
63/44 42132

NASA TECHNICAL MEMORANDUM

NASA TM-82414

SOLAR ENERGY ABSORPTION CHARACTERISTICS AND THE
EFFECTS OF HEAT ON THE OPTICAL PROPERTIES OF
SEVERAL COATINGS

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April 1981



NASA

*George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama*

TECHNICAL REPORT STANDARD TITLE PAGE

1. REPORT NO. NASA TM-82414		2. GOVERNMENT ACCESSION NO.		3. RECIPIENT'S CATALOG NO.	
4. TITLE AND SUBTITLE Solar Energy Absorption Characteristics and The Effects of Heat On The Optical Properties of Several Coatings				5. REPORT DATE April 1981	
				6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) J. R. Lowery				8. PERFORMING ORGANIZATION REPORT #	
9. PERFORMING ORGANIZATION NAME AND ADDRESS George C. Marshall Space Flight Center Marshall Space Flight Center, Ala. 35812				10. WORK UNIT NO.	
				11. CONTRACT OR GRANT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS National Aeronautics and Space Administration Washington, D.C. 20546				13. TYPE OF REPORT & PERIOD COVERED Technical Memorandum	
				14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES Prepared by Materials and Processes Laboratory					
16. ABSTRACT <p>This study was conducted to determine the solar energy absorption characteristics of several high-temperature coatings and to evaluate the effects of heat on these coatings. Included in the investigation were an electroplated alloy of black chrome and vanadium, electroplated black chrome, and chemically colored 316 stainless steel. The results of this study showed that each of the coatings possessed good selective solar energy absorption properties at laboratory ambient temperature. Measured at a temperature of 700°K (800°F), the emittances of black chrome, black chrome-vanadium, and colored stainless steel were 0.11, 0.61, and 0.15, respectively. Black chrome and black chrome-vanadium did not degrade optically in the presence of high heat [811°K (1000°F)]. Chemically colored stainless steel showed slight optical degradation when exposed to moderately high heat [616°K (650°F)], but showed more severe degradation at exposure temperatures beyond this level. Each of the coatings showed good corrosion resistance to a salt-spray environment.</p>					
17. KEY WORDS			18. DISTRIBUTION STATEMENT Unclassified-Unlimited		
19. SECURITY CLASSIF. (of this report) Unclassified		20. SECURITY CLASSIF. (of this page) Unclassified		21. NO. OF PAGES 13	
				22. PRICE NTIS	

PREFACE

This report records the results of the evaluation by Marshall Space Flight Center of various coatings and standard treatments of surfaces being designed as solar energy collectors. Although the investigation included both proprietary and non-proprietary electro-deposited coatings, this report does not constitute an endorsement of one product as opposed to another. It merely evaluates the properties of these coatings for the singular purpose of solar heating and cooling research.

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TECHNICAL MEMORANDUM

SOLAR ENERGY ABSORPTION CHARACTERISTICS AND THE EFFECTS OF HEAT ON THE OPTICAL PROPERTIES OF SEVERAL COATINGS

INTRODUCTION

Before solar energy can be directly utilized for heating and cooling buildings and heating water, it must be collected to produce a heating effect and the heat energy transferred to a working fluid. This is accomplished through the use of two basic types of collecting devices: flat plate and focused (or concentrator). A flat-plate collector consists of a transparent cover and a receiving surface or absorber. Solar energy is transmitted through the cover, absorbed, and the heat energy transferred to the working fluid. In the concentrator type, the solar energy is concentrated by passing it through a lens or reflecting it from a parabolic surface. The energy is focused on a collector tube (absorber) where extremely high temperatures may be produced and the absorbed heat energy transferred by the working fluid. Regardless of the type of collector, the receiving surface is a necessary component of the system and must absorb a large percentage of the sun's energy if good efficiency is to be achieved. These surfaces are usually prepared by reducing the solar energy reflectance (increasing the absorptance) of metals while maintaining their high infrared (IR) reflectivity (low emissivity). To produce such an optical change, black coatings are applied by electro-deposition or surfaces are blackened or colored by chemical change. The surface treatment or coating is controlled to a thickness sufficient to make the metal surface optically black yet thin enough to retain its high IR reflectance.

Since the receiving surface or absorber tube in the concentrator collector is subject to high heat, the tube material, as well as the absorber coating, must be able to withstand such heat for extended periods of time. This report presents the results of an investigation conducted to determine the optical effects of high heat on several absorber coatings. The plating parameters and optical characteristics of these coatings are also presented. Coatings known to have good optical properties but low resistance to heat were not included in the study.

EXPERIMENTAL PROCEDURE

The coatings were produced on metals and metal alloys by either electroplating or chemically treating the metal surface. In some cases, process parameters were varied in an effort to produce coatings with optimum solar energy absorption properties. After optimizing plating

parameters, the thermal stability of the coatings was evaluated by heating test panels in a furnace at varying temperatures up to 922°K (1200°F). Optical properties were measured before and after heating to determine the effect of the heat. If the solar energy absorption properties were still within an acceptable range after heating, the corrosion resistance of the coatings was determined. This was done by subjecting coated test specimens to a five-percent salt-spray environment controlled and operated in accordance with Mil-STD-810C, Method 509.1.

All optical measurements were made with either a Gier Dunkle Solar and IR Reflectometer, a Beckman DK-2A Ratio Recording Spectrophotometer, or a Willey 318S IR Spectrophotometer. The solar energy absorptances were determined by computing the difference between the solar energy reflectance and unity; the emittances were determined similarly by computing the difference between the IR reflectance and unity.

DISCUSSION AND RESULTS

Black Chrome

Black chrome is an electroplated coating which is usually jet black in appearance and composed of around 75 percent chromium and 25 percent chromium oxide. The plating parameters, corrosion resistance, and "as plated" optical characteristics of this coating were presented in a previous report [1] and will not be repeated except to present the optical effects of high heat on the coating. The emittance at 700°K (800°F), which was not measured in the previous study, was 0.11 as shown in Table 1.¹ The infrared reflectance curve used to obtain this value is shown in Figure 1.

TABLE 1. HIGH TEMPERATURE EMITTANCE - 700°K (800°F)

Black Chrome	0.11
Black Chrome Vanadium	0.61
Blackened Stainless Steel	0.15

The results of heat tests on plated low-carbon steel test specimens showed that temperatures up to 811°K (1000°F) did not significantly affect the optical properties of this coating. However, a sharp increase in emittance occurred upon exposure to a temperature of 922°K (1200°F) as shown in Table 2. Temperatures in the range of 700°K (800°F) to 811°K (1000°F) caused a drop in the absorptance but further heating at 922°K (1200°F) caused an increase in this property as also shown in the table. In appearance, test panels changed to a dull black which would suggest the observed increase in both solar energy absorptance and emittance.

1. The absorptances and emittances shown in Tables 1, 2, and 3 are average values obtained from duplicate test panels.

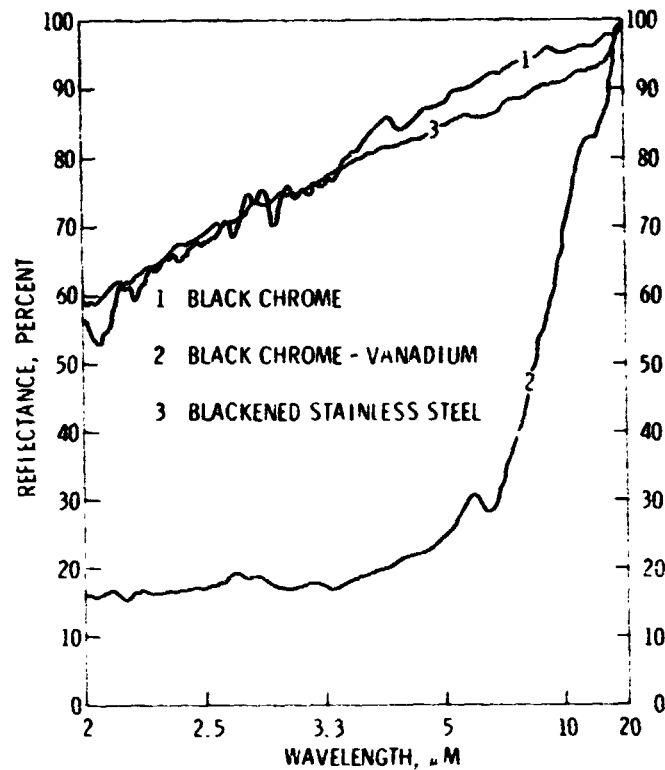


Figure 1. Infrared spectral reflectance of solar energy absorption coatings at 700°K (800°F)

TABLE 2. EFFECT OF HEAT ON SOLAR ENERGY ABSORPTION CHARACTERISTICS

Optical Properties	Before Exposure	Exposure Temperature, K°(F°)			
		616°K 650°F	700°K 800°F	811°K 1000°F	922°K 1200°F
Black Chrome					
Absorptance	0.94	0.91	0.90	0.87	0.95
Emittance	0.09	0.07	0.07	0.06	0.64
Black Chrome-Vandadium					
Absorptance	0.87	0.90	0.89	0.93	0.91
Emittance	0.29	0.18	0.19	0.17	0.30
Chemically Blackened Stainless Steel					
Absorptance	0.90	0.84	0.72	0.68	0.75
Emittance	0.11	0.12	0.12	0.14	0.25

NOTE: Exposure Time - 6 hours per heat cycle.

Black Chrome-Vanadium

This coating is an alloy reportedly composed of approximately 90 percent chromium and 9 percent vanadium and the oxides of the two metals [2]. The vanadium is present primarily as vanadium trioxide (V_2O_3) with only a small portion of the metal present. The chromium is primarily present as metal with only a small percentage of chromium oxide. The coating is produced by electrodeposition and is normally jet black in appearance. It reportedly has good adherence to substrates and excellent stability at elevated temperatures. When plated to conventional thicknesses, the coating exhibited a high thermal emittance and solar energy absorptance. In this study, coating thicknesses were reduced to lower the emittance yet maintain the high absorptance to furnish optical selectivity.

After conventional cleaning, test specimens of low carbon steel were first bright nickel plated to a thickness of 0.0127 mm (0.0005 in.) to furnish both corrosion protection of the substrate and a lower emittance base upon which to electroplate the black chrome-vanadium alloy. The black chrome-vanadium was then plated in a bath with the following composition:

Chromic Acid (CrO_3)	200 g/l (3.59 oz/gal)
Ammonium Metavanadate (NH_4VO_3)	10 g/l (1.34 oz/gal)
Glacial Acetic Acid (CH_3COOH)	6.5 ml/l (0.84 fluid oz/gal)

The bath was operated at a current density of 500 mA/cm² (500 A/ft²) and within a temperature range of 302°K (84°F) to 323°K (122°F).

Although plating time was varied in an effort to produce a coating with the optimum solar energy absorption characteristics, times of 3 to 5 min produced the optimum coating thicknesses with regard to optical selectivity. Such coatings showed laboratory ambient temperature absorptance and emittance values ranging from 0.84 to 0.90 and 0.27 to 0.41, respectively. The emittance of this coating, measured at 700°K (800°F), was 0.61. This value was derived from the infrared reflectance data produced by the Willey Spectrophotometer and shown in Table 1 and Figure 1. This emittance was unexpectedly high in view of the fairly low value exhibited by black chrome. Apparently the optical characteristics at this temperature were influenced by the presence of the vanadium or vanadium oxide in the alloy.

The reflectance at laboratory ambient temperature in the shorter wavelength (a small portion of the infrared, the visible light, and a small portion of ultraviolet) region of the energy spectrum is shown in Figure 2. At this temperature, and in this region, this coating is very similar to black chrome.

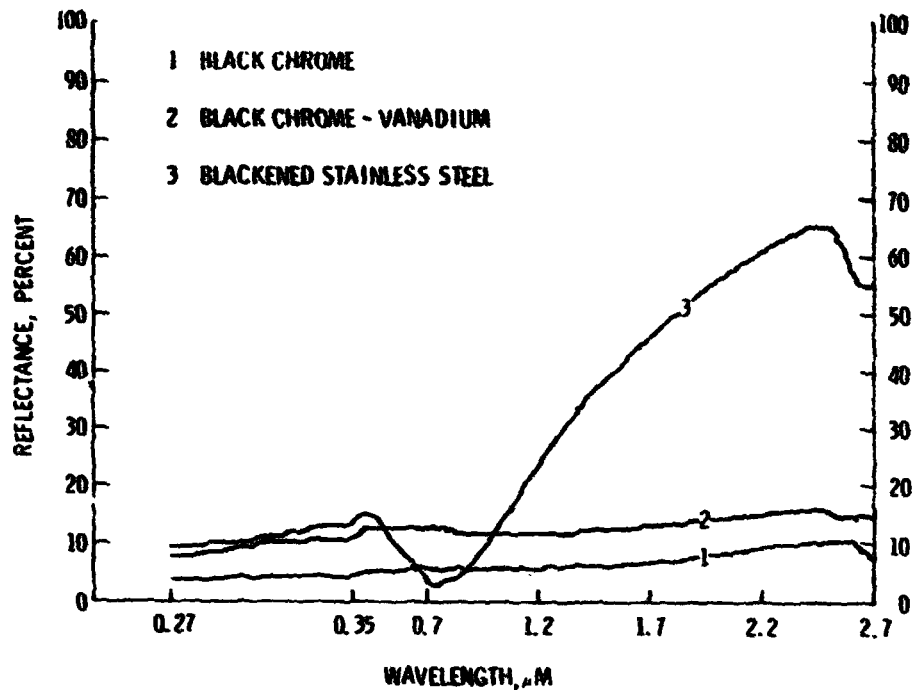


Figure 2. Spectral reflectance of solar energy absorption coatings (laboratory ambient temperature).

The results of heat tests showed that high temperatures did not significantly affect the optical selectivity of this coating. The absorptances and emittances fluctuated somewhat with the heat cycles, but at the end of the final heat period these values were only slightly higher than the original values as shown in Table 2. No significant change in appearance was observed as a result of the heat exposure.

Tests conducted to determine the corrosion resistance of this alloy showed that the coating had good resistance to a salt-spray environment. Test panels showed no significant corrosion when subjected to this environment for a period of 576 hr. As shown in Table 3 a slight decrease in both solar energy absorptance and emittance was noted which probably resulted from minor stains on the panel surfaces. These stains were caused by an edge corrosion product running down onto the main test surface of the panel. This edge corrosion was initiated at points where electrical contact was made during the electroplating.

Colored Stainless Steel

Various colored films (including black) can be produced on the surfaces of stainless steel by immersion in mixtures of sulfuric and chromic acid. The different colors are produced by varying the treatment time in the acid mixture. The "as formed" film is relatively soft but may be hardened by a process developed, in recent years, by the International Nickel Co., Inc. [3]. This process employs the cathodic

**TABLE 2. EFFECT OF SALT-SPRAY ENVIRONMENT ON
SOLAR ENERGY ABSORPTION CHARACTERISTICS**

Optical Properties	Before Exposure	After Exposure
<u>Black Chrome</u>		
Absorptance	0.93	0.93
Emittance ^a	0.13	0.13
<u>Black Chrome-Vanadium</u>		
Absorptance	0.90	0.87
Emittance ^a	0.17	0.13
<u>Chemically Blackened Stainless Steel</u>		
Absorptance	0.83	0.88
Emittance ^a	0.12	0.12

a. Laboratory ambient temperature.

NOTE: Exposure time -- 576 hrs.

treatment of the colored film in a chromic and phosphoric acid mixture. Test panels of 316 stainless steel utilized in this program were colored (blackened) and subsequently hardened in these baths (reported in Reference 3). The composition and operating conditions of the baths are listed below:

Coloring Solution

Chromic Acid	250 g/l (22.5 oz/gal)
Sulfuric Acid	400 g/l (65.7 oz/gal)
Operating Temperature	353°K (176°F) to 358°K (185°F)

Hardening Solution

Chromic Acid	250 g/l (22.5 oz/gal)
Phosphoric Acid	2.5 g/l (.34 oz/gal)
Operating Temperature	ambient
Time	10 min
Current Density	2.8 mA/cm ² (2.6 A/ft ²)

For the purpose of this program, the processing time in the coloring solution was controlled to produce a black coating with as high a solar energy absorptance and as low a thermal emittance as possible. Immersion times were varied from 5 to 13 min (no significant film was formed during the first 5 min), but it appeared that around 8 to 9 min in the acid mixture produced a film with the most desirable solar energy absorption properties. Panels treated for this length of time showed laboratory ambient temperature solar energy absorptances and thermal emittances in the range of 0.87 to 0.93 and 0.14 to 0.26, respectively. The emittance of the coating, measured at 700°K (800°F), was 0.15 as shown in Table 1 and Figure 1. This value was almost as low as that of black chrome and there was somewhat less fluctuation in reflectance as noted by the two curves.

At laboratory ambient temperature in a portion of the ultraviolet and visible region (wavelength range of 0.27 to 0.35) of the spectrum, the reflectance of this coating was slightly higher than either the black chrome or the black chrome-vanadium alloy as shown in Figure 2. However, in the outer visible region, the blackened stainless steel showed a sharp decrease in reflectance just prior to a sharp increase beginning with and continuing into the infrared. These data are shown in Figure 2.

The results of heat tests showed that the laboratory ambient temperature optical properties of this coating were degraded by exposure to heat. A slight decrease in solar energy absorptance occurred from exposure to moderately high heat, but more severe degradation occurred with increase in exposure temperatures. These data are shown in Table 2. The appearance of test panels changed from an initial bluish black to a brownish black after the initial heat period. Further heating at higher temperatures caused severe fading of the black chemical coating. Still further heating caused the surface of the substrate to become re-blackened from oxidation in the high-temperature air. This oxidation probably caused the observed increase in both the absorptance and emittance after the 922°K (1200°F) heat cycle as shown in the table.

Tests conducted to determine the corrosion resistance of this alloy showed that the chemically blackened stainless steel had excellent resistance to a salt-spray environment. As shown in Table 3 test panels had no corrosion or change in optical properties after subjection to this environment for a period of 576 hr.

CONCLUSIONS

The results of this study showed that the laboratory ambient temperature solar energy absorption properties of electroplated black chrome and black chrome-vanadium alloy were degraded less by exposure to high heat than chemically blackened stainless steel. However, the thermal emittance of the black chrome-vanadium alloy, measured at 700°K (800°F), was considerably higher than that of the black chrome and chemically blackened

stainless steel measured at the same temperature. Each of the three coatings showed good corrosion resistance to a salt-spray environment. Based on these results, it appears that each coating would have some specific use in absorbing solar energy. Because of the effect of the high heat on the chemically blackened stainless steel and the high emittance (at an elevated temperature) exhibited by the chrome-vanadium, it appears that black chrome would be more suitable for use in concentrator solar energy collectors where temperatures may be in the 616°K (650°F) to 700°K (800°F) range. On the other hand, the use of chrome-vanadium and chemically blackened stainless steel would be limited to lower temperature collectors. It should be noted that in this study only a cursory look was taken at the optical effects of heat on these coatings. The results invite a more exhaustive examination, one which might include subjecting the coatings to moderately high heat for extended periods of time, and heat tests that would continually cycle the coatings from high heat to ambient temperature.

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APPROVAL

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The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.



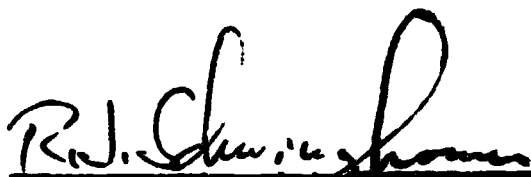
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